

## High-Pressure Phase Equilibria of Binary and Ternary Systems with Ionic Liquids

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Ionic liquids have been recognized as solvents with a big potential for all kind of technological applications, especially in combination with supercritical solvents. In order to design useful applications, knowledge of the phase behavior of binary and ternary systems with ionic liquids and supercritical fluids are a prerequisite. In this contribution, the phase behavior of a number of binary systems of ionic liquids with supercritical fluids like carbon dioxide ( $\text{CO}_2$ ), trifluoromethane ( $\text{CHF}_3$ ), ethane ( $\text{C}_2\text{H}_6$ ) and hydrogen ( $\text{H}_2$ ) will be discussed. The ionic liquids were selected from the homologous series 1-alkyl-3-methylimidazolium hexafluorophosphate ([alkylmim][ $\text{PF}_6$ ]), 1-alkyl-3-methylimidazolium tetrafluoroborate ([alkylmim][ $\text{BF}_4$ ]) and 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([alkylmim][ $\text{Tf}_2\text{N}$ ]). Emphasis was given to the systematic changes in phase behavior as a function of the length of the alkyl group. For the binary systems consisting of either  $\text{CO}_2$  or  $\text{CHF}_3$  with [alkylmim][ $\text{PF}_6$ ], the three-phase equilibria were also measured up to their critical endpoints. The experimental results obtained show that the binary systems of  $\text{CO}_2$  or  $\text{CHF}_3$  [alkylmim][ $\text{PF}_6$ ] most likely will have Type-III fluid phase behavior according to the classification of Scott and Van Konynenburg. A major conclusion that could be drawn from this study is that significant amounts of the ionic liquid can be present in the vapor phase in case  $\text{CHF}_3$  is used as the supercritical fluid. An explanation for this behavior will be discussed. Furthermore, the systematic in complex fluid multi-phase behavior in the ternary systems of  $\text{CO}_2$  [ $\text{bmim}$ ][ $\text{BF}_4$ ] methanol and  $\text{CO}_2$  [ $\text{bmim}$ ][ $\text{BF}_4$ ] isopropanol will be discussed.